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ANALYTICAL SCIENCES MARCH 2000, VOL. 16

Electrothermal Atomic Absorption Spectrometric Determination of Cadmium after Coprecipitation with Nickel Diethyldithiocarbamate

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Nickel diethyldithiocarbamate (nickel DDTC) coprecipitated quantitatively 3 - 90 ng of cadmium in up to 500 cm^3 of the sample solution at pH 4.0 - 11.5. The coprecipitant could be easily dissolved with nitric acid (1+1) and acetone, and 3 - 90 ng of cadmium in the final solution (10 cm^3) could be determined by electrothermal atomic absorption spectrometry. The peak height of cadmium in atomic absorbance measurements remained almost constant, even if large amounts of nickel DDTC (up to at least 10 mg as nickel amount) were used for the coprecipitation. The detection limit (signal/noise=2) was 1.2 pg cm^{-3} of cadmium in 500 cm^3 of the initial sample solution. The 32 diverse ions investigated did not interfere with the determination in at least a 1000-fold mass ratio to cadmium. The proposed method was successfully applied to the determination of trace amounts of cadmium in river and sea water.

(Received November 1, 1999; Accepted December 20, 1999)

Coprecipitation has been widely used for the preconcentration of trace cadmium in water, associated with various determination techniques. In combination with electrothermal atomic absorption spectrometry, which is prone to suffer from a matrix effect, it is desirable to use such a coprecipitant so that the separation factor for the alkali and alkaline earth metals is sufficient, and the presence of the coprecipitant, itself, does not cause background absorption. This time, we have recognized that nickel diethyldithiocarbamate (nickel DDTC), which has been proposed to be a coprecipitant for lead,[1] is an excellent collector for trace amounts of cadmium, and hardly coprecipitates matrix ions, such as alkali and alkaline earth metals; also, the use of nickel DDTC does not cause interference in the electrothermal atomic absorption spectrometric determination of cadmium. Further, this coprecipitant can be easily dissolved with nitric acid (1+1) and acetone without any digestion or heating, thus suggesting a simple procedure for cadmium determination.

For the preconcentration of cadmium prior to an electrothermal atomic absorption spectrometric determination, several coprecipitants, such as hydroxides of iron(III),[2] hafnium,[3] and indium,[4-7] pyrrolidinedithiocarbamate (APDC) of cobalt,[8] copper,[9,10] and iron(III),[9,10] and zinc DDTC,[11,12] have been proposed up to now. However, the method using iron(III) hydroxide[2] can not avoid the coprecipitation of large amounts of alkaline earth metals, which may interfere with the cadmium determination. Also that using hafnium hydroxide is expensive. Although indium hydroxide[3-6] is an excellent collector, indium, itself, causes serious background absorption. Thus, to eliminate background absorption, the minimal amount of indium used,[4,6] and the volatilization of indium as bromide during the ashing stage in the presence of thiourea,[5,7] have been tried. The use of cobalt APDC[8] requires a long digestion of the precipitate in order to simplify the sample matrix. APDC of copper and iron(III)[9,10] and zinc DDTC[11,12] is also dissolved only slowly. The method proposed here overcomes those weak points. This paper describes the fundamental conditions for the coprecipitation of trace amounts of cadmium in water with nickel DDTC and for an electrothermal atomic absorption spectrometric determination of cadmium.

Experimental

Apparatus

A Hitachi 170-70 Zeeman atomic absorption spectrometer with a Hitachi cadmium hollow-cathode lamp was used for atomic absorption measurements. The optimum operation conditions, which were studied using a solution obtained by coprecipitation according to the recommended procedure from a distilled water containing 50 ng of cadmium, are summarized in Table 1. For the pH measurements, a Toa Model HM-5BS glass-electrode pH meter was used.

Reagents

Cadmium and nickel solutions. A solution containing about 1 mg cm^{-3} of cadmium or nickel was prepared by dissolving guaranteed reagent-grade metal nitrate in a small amount of

Table 1 Operating conditions for atomic absorption spectrometry

Analytical wavelength	228.8 nm
Lamp current	10 mA
Slit width	No. 3 (2.2 nm)
Argon gas flow rate	
Sheath gas	3 dm^3 min^{-1}
Carrier gas	0 dm^3 min^{-1}
Injection volume	10 mm^3
Cuvette	uncoated tube type graphite furnace
Drying conditions	21 A (*ca.* 150°C), 40 s
Ashing conditions	50 A (*ca.* 400°C), 90 s
Atomizing conditions	180 A (*ca.* 2000°C), 5 s

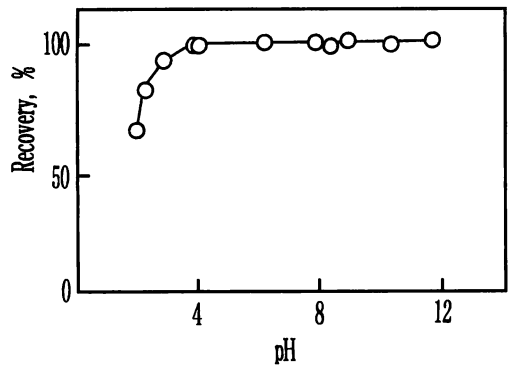

Fig. 1 Effect of the pH on the recovery of cadmium from about 100 cm³ of sample solution containing 50 ng of cadmium according to the recommended procedure.

Table 2 Effect of diverse ions on the determination of 50 ng of cadmium

Mass ratio[a] [Ion] / [Cd]	Ion
1200000	Na^+
1000000	Cl^-
500000	K^+
250000	Mg^{2+}, Ca^{2+}
100000	Br^-, I^-, SO_4^{2-}
10000	F^-
2000	PO_4^{3-}
1000	Li^+, Sr^{2+}, Ba^{2+}, Al^{3+}, Ga^{3+}, In^{3+}, Sn^{4+}, Pb^{2+}, Sb^{3+}, Bi^{3+}, Cu^{2+}, Zn^{2+}, La^{3+}, Ce^{3+}, Zr^{4+}, Th^{4+}, Mo^{VI}, W^{VI}, Cr^{3+}, Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}

The coprecipitation was carried out from about 80 cm³ of the solution at a pH of about 9.
a. The errors are within ±5%.

concentrated nitric acid and diluting with distilled water. The concentrations of both cadmium and nickel were determined by chelatometric titration using Xylenol Orange and Murexide as indicators, respectively.

DDTC solution. About a 2% DDTC solution was prepared by dissolving sodium salt of DDTC (Wako, AAS-reagent grade) in distilled water and filtering out any insoluble material.

All other reagents used were of guaranteed reagent grade.

Recommended procedure

To a sample solution (up to 500 cm³) containing 3 - 90 ng of cadmium, 3 mg of nickel is added, followed by 2 cm³ of 2% DDTC solution with stirring. The pH of the solution is adjusted to about 9 with aqueous ammonia (1+2), measuring it with a pH meter. After the solution is allowed to stand for a few minutes, the precipitate is collected on a 3G4 sintered-glass filter and washed with a small amount of distilled water. Then, 1 cm³ of nitric acid (1+1) is poured onto the precipitate. In the nitric acid (1+1), the precipitate is partially dissolved, turning its color gradually from yellowish-green to brown. A few minutes later, 1 cm³ of acetone is added for complete dissolution of the precipitate; a solution is then made up to 10 cm³ with distilled water. The atomic absorbance of cadmium is measured under the operating conditions given in Table 1. A blank using distilled water is run according to the same procedure as for the sample solution.

Results and Discussion

Study of the optimum conditions for coprecipitation

Effect of pH on coprecipitation. The effect of the pH on the coprecipitation with nickel DDTC was studied with a solution containing 50 ng of cadmium. As the results shown in Fig. 1, the maximum and almost constant recoveries were obtained in the pH range 4.0 - 11.5. The precipitate of nickel DDTC obtained above a pH of about 8 was bulky, and hence easily handled. Therefore, the pH was adjusted to about 9.0 with aqueous ammonia (1+2) in further experiments.

Effect of the amount of coprecipitant. According to the recommended procedure, the necessary amount of nickel DDTC for coprecipitation was examined with a sample solution (50 - 500 cm³) containing 50 ng of cadmium. The required amount of nickel DDTC for the quantitative coprecipitation increased along with increasing the sample volume; also, complexation of 2 mg of nickel with DDTC was necessary for more than 300 cm³ of the sample solution. Since the atomic absorption of cadmium was not affected even if 10 mg of nickel was used for the coprecipitation, 3 mg of nickel was used in subsequent experiments.

Effect of the amount of DDTC. The use of up to at least 10 cm³ of a 2% DDTC solution slightly affected the cadmium absorption. DDTC reacts with nickel to form a 2:1 complex. Thus, 2 cm³ of a 2% DDTC solution, which corresponds to about 3-times (as a mole ratio) of 3 mg of nickel, was used.

Effect of the standing time of the precipitate. The recovery of cadmium was hardly influenced by the standing time of the precipitate. Thus, an almost complete recovery was obtained from a few minutes to at least 3 h of standing.

Dissolution of nickel DDTC. The precipitate of nickel DDTC did not dissolve completely in common mineral acids at room temperature. However, we have recognized that the precipitate easily dissolved without any heating, adding nitric acid (1+1), followed by the addition of acetone a few minutes later. In nitric acid (1+1), the precipitate dissolved partially, turning its color gradually from yellowish-green to brown. By the addition of acetone, it dissolved completely, with the solution becoming colorless turbid at first, and then clear within a few minutes. Both the colorless turbid and clear solutions did not cause any serious background absorption, and could be used to measure the atomic absorbance of cadmium.

An adequate concentration range of nitric acid for the dissolution of the precipitate was 5 - 10 mol dm^{-3}, and the necessary amount of acetone was more than 0.5 cm³. When concentrated nitric acid was added, the precipitate changed color from yellowish-green to brown, but did not dissolve in acetone. In the case of diluted nitric acid, the precipitate remained unchanged as it was, and also did not dissolve in acetone. In this experiment, 1 cm³ each of nitric acid (1+1) and acetone was used for dissolution of the precipitate, since the addition of 0.5 - 4 cm³ of nitric acid (1+1) and up to 4 cm³ of acetone did not affect the cadmium absorption.

Calibration curve

A straight line passing through the origin was obtained from 3 to 90 ng of cadmium in the final solution (10 cm³) using the recommended procedure. This calibration curve was almost the same as that which was prepared without the coprecipitation procedure, using a standard solution containing various amount of cadmium, 3 mg of nickel, 2 cm³ of 2% DDTC solution, 1 cm³

Table 3 Recovery of cadmium from spiked water samples

Sample volume/cm^3	Cd added/ ng	Cd found/ ng	RSD, %
River water[a]			
500	3	2.9_5	14.3
500	90	88.7	5.5
Tap water[a]			
500	3	2.86	11.9
500	90	89.9	6.2
Sea water			
500	3	2.9_1[b]	13.7
500	90	86.9[b]	6.3

The recoveries obtained are the average of three replicate determinations.
a. Amounts of cadmium in river and tap water were less than the detection limit of the proposed method.
b. Recoveries of cadmium were calculated by subtracting the peak height due to sea water alone from one due to sea water spiked with cadmium.

Table 4 Results of the determination of cadmium in river and sea water

Location of sampling point	Calibration method	Standard addition method
	Cd found/ ng cm^{-3}	Cd found/ ng cm^{-3}
Kakehasi river		
Shorenji	0.088	0.092
Yusenji	0.048	0.044
Nomiohashi	0.040	0.044
Seashore		
Kanaiwa	0.025	0.028
Ohno	0.019	0.023
Uchinada	0.026	0.023

The results obtained are the average of duplicate determinations. The sample volume taken was 300 cm^3.

of nitric acid (1+1), and 1 cm^3 of acetone in 10 cm^3. The relative standard deviation was 5.52% for 50 ng of cadmium in about 300 cm^3 of the sample solution (four determinations); and the detection limit (signal to noise ratio of two) was 1.2 pg cm^{-3} of cadmium in 500 cm^3 of the initial sample solution.

Interferences

The influence of 33 diverse ions was studied using 50 ng of cadmium in about 80 cm^3 of the sample solution. Table 2 shows that large amounts of sodium, potassium, magnesium, calcium, fluoride, chloride, bromide, iodide, sulfate, and phosphate did not interfere with the determination. No other ions tested produced any serious interference effect, even at a concentration 1000-times the mass of the cadmium present.

Recovery of cadmium from spiked water samples

The utility of the present method was evaluated by examining the recovery of cadmium from river, tap, and sea water samples spiked with cadmium. The obtained results are given in Table 3, indicating that the proposed method is applicable to analyses of water samples containing down to 6 pg cm^{-3} of cadmium in 500 cm^3 of the initial sample solution.

Based on the results obtained from above experiments, the determination of cadmium in river and sea water (located in Ishikawa prefecture) was tried. The samples were filtered through a Toyo Roshi TM-2p membrane filter (pore size 0.45 μm) and analyzed as soon as possible after sampling. As shown in Table 4, the results obtained by the calibration and standard addition methods were in good agreement.

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